PIER Energy-Related Environmental Research
Environmental Impacts of Energy Generation, Distribution and Use

Trihalomethane Formation in Treated Cooling Water

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The Issue

The term trihalomethanes (THMs) refers to four harmful compounds that form in water when a halogen—chlorine or bromine—reacts with dissolved organic carbon compounds, such as those formed by plant decay. Trihalomethanes are present in virtually all chlorinated water supplies, including those used for power plant cooling.

Trihalomethanes (THMs)	
Trichloromethane (chloroform)	$CHCl_3$
Dibromochloromethane	$CHClBr_2$
Bromodichloromethane	$CHCl_2Br$
Tribromomethane (bromoform)	$CHBr_3$

These four semi-volatile compounds are byproducts of disinfecting water with chlorine or bromine.

Most power plants that employ wet cooling systems use chlorine to prevent biofouling, which raises concerns that individuals who work around these systems could receive harmful exposure to THMs—particularly through inhalation and skin absorption. Several studies of once-through cooling systems with intermittent chlorination have indicated that TMH levels may be high enough to be cause for concern. However, little or no research has been conducted to study THM formation in cooling towers. Data on the formation and concentration of THMs in cooling towers are needed to address this occupational health issue.

THMs are suspected to cause not only cancer, but also liver and kidney damage, retarded fetal growth, birth defects, and possibly miscarriage. The U.S. Department of Health and Human Services has determined that chloroform, a THM, may reasonably be anticipated to be a carcinogen.[1] In addition, breathing a level of 900 parts chloroform per million parts air (900 ppm) for even a short time can cause dizziness, fatigue, and headache; and liver and kidney damage can result from breathing air, eating food, or drinking water containing high levels of chloroform for long periods of time.[2] The Occupational Safety and Health Administration (OSHA) has set the maximum allowable concentration of chloroform in workroom air during an 8-hour workday in a 40-hour week at 50 ppm.[3]

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[1] Agency for Toxic Substances and Disease Registry. September 1997. *ToxFAQs™ for Chloroform.* www.atsdr.cdc.gov/tfacts6.html.
[2] Ibid.
[3] Ibid.

Exposure to THMs can come from ingestion (e.g., drinking water), inhalation (e.g., from showering or workplace exposure), or from absorption through the skin contact (e.g., from swimming in chlorinated water or from water vapor in the air). Although most research has focused on the health effects of THMs in drinking water, ingestion does not appear to be the primary route of exposure. One study funded by the Centers for Disease Control found that people had higher levels of THMs in their blood after taking a 10-minute shower than after drinking a liter of tap water.[4] And a study on skin contact with volatile organic compounds (VOCs) concluded that skin absorption of VOCs, such as THMs, in drinking water is probably higher than previously thought.[5] Running showers using water from public chlorinated groundwater supplies can produce low levels (5 parts per billion) of volatilized THMs in adjoining rooms.[6] Power plant employees have a higher potential of exposure to THMs because of the constant mist generated by cooling towers.

Cooling towers, shown here, use significantly less water than traditional once-through wet cooling systems.

Use of degraded water as cooling tower makeup conserves freshwater supplies, but may increase THM formation due to higher organic content.

Almost all power plant cooling towers in the United States chlorinate circulating water; however, virtually no research has examined THM formation in cooling towers. The need for better assessment of THM formation in cooling towers is compounded by the increased use of chlorinated recycled water (i.e., tertiary treated effluent from wastewater treatment plants). California has mandated that recycled water be used for cooling when available, so it is being used increasingly for power plant cooling. Recycled water contains higher levels of organic carbon compounds than most freshwater supplies, which may lead to an even greater formation of trihalomethanes.

Moreover, cooling towers receive a significant amount of organic airborne matter (vegetation and insects) in the airstream, which could facilitate THM production. Based on known formation mechanisms, it is likely that THMs are formed in cooling towers and emitted in the airstream and in blowdown, and that power plant workers are exposed to those THMs, although just how much is unclear.

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[4] Wanjek, Christopher. March, 12, 2002. "In Virginia, Water Chlorination is Blamed for Miscarriages. Below the Surface, the Science on the Issue is Murky." *Washington Post.* p. F1.

[5] Brown, H. S., D. R. Bishop, and C. A. Rowan. 1984. "The Role of Skin Absorption as a Route of Exposure for Volatile Organic Compounds (VOCs) in Drinking Water." *American Journal of Public Health.* 74 (5): 479–484.

[6] May, S. J., P. A. Kostle, G. M. Breuer. 1993. *Comparison of Trihalomethanes in Residential Water Using Source Surface Water and Indoor Air with Residential Water Using Source Groundwater and Indoor Air.* University Hygienic Laboratory, University of Iowa.

Because California lists several THM compounds as carcinogenic and recognizes that long-term exposure to these compounds may also cause liver, kidney, and nervous system damage, it is essential that research establish safe practices for using treated recycled water for cooling.

Project Description

The project began with a literature review, which found no studies on TMH formation in cooling towers. Researchers then conducted field sampling and analysis at two power plants with cooling towers:

- Site 1 was cooled with fresh well water, using 12.5% sodium hypochlorite injected periodically—usually for 15 minutes once per day—to achieve a target level of free available chlorine residual of 0.2 mg/l. If the target was not sustained after two hours, the chlorine injection was repeated.
- Site 2 was cooled with a blend of 60%–65% fresh well water and 35%–40% reclaimed municipal effluent. Normally this plant used activated bromine for biological control, but the bromide feed system was not working at the time of the test, so the test results reflect continuous chlorination with 12.5% sodium hypochlorite to maintain a free available chlorine residual of 0.2–0.4 mg/l and total chlorine residual of 0.2–1.2 mg/l.

PIER Program Objectives and Anticipated Benefits for California

This project offers numerous benefits and meets the following PIER program objectives:

- **Providing environmentally sound and safe electricity.** By evaluating THM formation in wet cooling systems, this project helps to ensure that electricity is produced without occupational or public health risks from THM production as a result of water chlorination. This work will benefit not only the electricity industry, but also the many other industries that employ wet cooling.
- **Safe use of recycled water for cooling.** The Energy Commission has certified five power plants, totaling 1673 MW, that will use recycled water for cooling. It is anticipated that additional projects slated to use recycled water (consisting of thousands of additional megawatts of generation capacity) will be proposed in the future. This research will help power producers to operate effective cooling systems without risking the health of their workers. As a result, more facilities may turn to recycled water for cooling, thereby freeing freshwater supplies for other uses. This research should also be applicable to other industries using reclaimed water.

Results

TMH compounds were formed during halogenation at both sites, although the occupational exposure risk appears negligible.

The intermittent chlorination at Site 1 did not generate significant amount of total trihalomethanes (TTHM)—5 µg/l in the riser and 3 µg/l in the basin. These concentrations attenuated to nondetectable levels in the cooling water in less than two hours. Continuous halogenation at Site 2 generated detectable levels of TTHM on a continuous basis, but levels never exceeded 5 µg/l.

Site analysis found that approximately 80% of the TTHM escapes from the cooling tower in the airstream and the rest in blowdown (this finding is based on Site 2, as blowdown was valved off at Site 1, so presumably 100% of Site 1's TTHM escaped through the airstream). At both sites, calculated airstream concentrations of TTHM were very low and far below the OSHA threat level for chloroform. At Site 1, the average and maximum concentrations of TTHM in the airstream during the sampling period were calculated to be 0.00013 and 0.00022 ppb_{vol}, respectively. At Site 2 the average concentration of TTHM in the airstream during the sampling period was calculated to be 0.60 $\mu g/l_{vol}$. At Site 2, 10%–20% of the TTHM emitted in the airstream and blowdown originated from the cooling tower makeup, which comprised reclaimed water mixed with freshwater.

The study found that existing models for THM formation in domestic water supplies—where chlorine can be in contact with treated water for many hours or even days—are not applicable to cooling towers. Most power plants use periodic chlorination (from one to three times per day for 15- to 60-minute periods) to maintain effective biological control. Only a few power plants chlorinate continuously and maintain a low level of chlorine residual (usually less than 0.5 mg/l). However, existing models for evaluating THM formation in drinking water supplies assume constant low-level chlorination; thus, new models that evaluate formation in periodic chlorination systems must be developed.

Moreover, a new "cooling tower" THM model would have to take into account recirculating water and the continuous removal of THMs from the airstream. New models should specifically address the following:

- Intermittent chlorination and/or bromination for systems using freshwater to model low-level THM formation and attenuation
- Continuous chlorination and/or bromination for systems using treated municipal effluent to model steady/residual levels of THMs and their continuous release to the airstream

Final Report

The final report on the results of this work, *The Formation and Fate of Trihalomethanes in Power Plant Cooling Water Systems* (CEC-500-04-035), is posted on the Energy Commission website at www.energy.ca.gov/reports/2004-05-26_500-04-035.PDF.

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